

EFFECT OF MECHANICAL GRINDING AND IONIC LIQUID PRE-TREATMENT ON OIL PALM FROND

(Kesan Pra-rawatan Pengisaran Mekanikal dan Cecair Ionik ke atas Pelepah Kelapa Sawit)

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Abstract

The present study was set to investigate the chemical structural group of different particle size of Oil palm frond (OPF) after mechanical and Ionic liquid (IL) pretreatment by FTIR analysis. The particle sizes range of biomass used were 0-75, 75-125, 125-180, 180-250 and 250-355 μm which were prepared through mechanical grinding process by using an analytical mill. IL used in this experiment was 1-ethyl-3-methylimidazolium chloride [EMIM][Ac] with two different concentration of 1M and 3M. Pretreatment by IL was done on BioshakeIQ for 3 hours at 800 rpm and 85 °C. The pretreated OPF was then analyzed using FTIR spectroscopy in order to evaluate the performance of mechanical grinding and IL pretreatment based on the change observed in chemical structure through functional group existed. It was found that after size reduction through grinding process, the spectra between all particle sizes obtained did not differ much except for particle size range of 75-125 μm . The particle size range showed on much characteristics of cellulose due to the broad peak within the 3600-3100 cm^{-1} which stand for O-H bonding. However, when the FTIR spectra were compared between before and after IL pretreatments, there were some different in peaks trend which explained there were some chemical structure changes within the OPF samples. There were some appearances and disappearances of certain peak were observed after the IL pretreatment especially the peak at band near 1700 cm^{-1} and 1550 cm^{-1} .

Keywords: Mechanical pretreatment, Ionic liquid, lignocellulosic biomass, bioethanol, cellulose, oil palm frond

Abstrak

Kajian ini dijalankan untuk mempelajari kumpulan struktur kimia dari pelepah kelapa sawit (OPF) selepas pra-rawatan mekanikal dan cecair ionik (IL) dengan menggunakan analisis FTIR. Julat saiz zarah biomas yang digunakan adalah 0-75, 75-125, 125-180, 180-250 dan 250-355 μm yang disediakan melalui proses pengisaran mekanikal. IL yang digunakan dalam penyelidikan ini adalah 1-etil-3-methylimidazolium asetat [Emim][Ac] dengan dua kepekatan berbeza iaitu 1M dan 3M. Pra-rawatan dengan IL dilakukan menggunakan BioshakeIQ selama 3 jam pada 800 rpm dan 85°C. Selepas pra-perawatan, OPF dianalisis menggunakan spektroskopi FTIR bagi menilai potensi pra-rawatan berdasarkan perubahan yang diperhatikan melalui kumpulan struktur kimia yang wujud sebelum dan selepas pra-rawatan. Berdasarkan keputusan selepas pengurangan saiz melalui proses pengisaran, spectrum dari analisis FTIR antara semua saiz zarah yang diperolehi tidak banyak berbeza kecuali saiz 75-125 μm . Saiz tersebut menunjukkan banyak ciri-ciri selulosa berbanding saiz lain berdasarkan puncak yang luas dalam lingkungan 3600-3100 cm^{-1} melibatkan ikatan OH. Apabila spektrum FTIR dibandingkan antara sebelum dan selepas pra-rawatan IL, perbezaan dapat dilihat antara puncak yang terbentuk di antara satu sama lain yang menjelaskan terdapatnya beberapa perubahan struktur kimia. Ada beberapa puncak yang sebelum dilakukan pra-rawatan menggunakan IL wujud tetapi, setelah pra-rawatan dijalankan hilang terutama yang terbentuk berhampiran 1700 cm^{-1} dan 1550 cm^{-1} .

Kata kunci: Prarawatan mekanikal, Cecair ionik, biojisim lignoselulosa, bioetanol, selulosa, pelepah kelapa sawit

Introduction

In recent years, non-renewable energy resources especially the petroleum are facing challenges in depleting reserves, increasing price and environmental issue. Therefore, it is critically important to explore new alternatives to replace the petroleum-based liquid transportation fuels. One such alternative is bioethanol produce from

lignocellulosic biomass (LB). The LB, second generation of biofuel which come from the woody biomass is a promising raw material for biofuel/bioethanol production. It is sustainable, relatively carbon neutral and readily available with a yearly supply of approximately 200 billion tons worldwide [1].

However, conversion of LB to bioethanol which comprising of hydrolysis, fermentation and separation processes is facing with chemical and physical barriers. More specifically, crystalline structure of cellulose, presence of lignin and covalent cross-linkages between hemicellulose and lignin which wrapped around the cellulose in cell wall interrupt the digestibility of cellulose during enzymatic hydrolysis to release sugar [2]. A high sugar yield in this processing step is important to the cost-effectiveness in production of cellulosic bioethanol. Hence, pretreatment is the key to unlock the recalcitrance of LB during the hydrolysis and downstream fermentation of the sugars released [1].

To date, several pretreatment approaches have been introduced to improve the LB accessibility to enzymatic hydrolysis including physical (milling, grinding etc.), chemical (organosolv, acid, alkali etc.), physico-chemical (wet oxidation, ammonia fiber explosion, steam explosion etc.) and biological pretreatment [3]. However, most of the conventional pretreatment methods suffer from one or more drawbacks like high energy consumption, costly, toxicity and instability in processing. As for example, pretreatment by dilute acid requires costly corrosion resistant equipment and also produce a significant amount of fermentation inhibitors during the processing step.

Recent attempts have been striving to make pretreatment methods cost effective, environmental friendly and more efficient. Among them, application of ionic liquid (IL) as a chemical solvent in pretreatment method has attracted much attention. IL is an organic salt comprising of cations and anions which melt below 100°C [4]. The safety features of IL which is unique and only requires mild process condition during the pretreatment are regarded as the main advantages [4]. Furthermore, the biomass structure after pretreatment by IL has altered its native structure. It also resulted in higher saccharification with better digestibility compared to untreated biomass during the enzymatic hydrolysis [2]. Although the IL has ability to alter the biomass structure and able to dissolve the cellulose in the biomass, however, its effectiveness during the pretreatment processing step also will depends on the particles size of biomass. Previously study was stated that the smaller the particles size, the larger the total surface area, thus, more surface area contacted between biomass with IL solvent during the pretreatment. As a result, cellulose is easier to dissolve and its digestibility during the enzymatic hydrolysis step also will be enhanced [5].

In this study, Oil palm frond (OPF) was undergone some sort of mechanical grinding pretreatment to produce different particles size and then were pretreated using 1-ethyl-3-methylimidazolium acetate [EMIM][Ac] with two different molarity. Chemical structure of every particles size will be investigated before and after pretreatment in order to prove the contribution of particle size during the pretreatment by IL. Besides, the performance of IL also was evaluated based on the change observed in chemical structure of the biomass.

Materials and Methods

Materials

Oil palm frond (OPF) was supplied by Forest Research Institute of Malaysia (FRIM) located in Kepong, Kuala Lumpur. Ionic liquid (IL) used in this experiment was 1-ethyl-3-methylimidazolium acetate [EMIM][Ac] supplied by Sigma-Aldrich, Malaysia. The IL was in liquid form with 90% purity, molecular weight of 170.21 g/mol and density of 1.027 g/cm³.

Mechanical pretreatment (grinding)

The OPF was dried in a universal oven (ULE 400, Memmert) at 60 °C for 48 hours. The dried biomass then was placed in a desiccator and allowed to cool down to room temperature. The biomass then cut into smaller size before being grinded by a manual grinder machine (IKA A11 basic Analytical mill 115V, IKA Germany). The grinded samples were sieved by using a sieve shaker (Endecotts Octagon Digital) into different size range for 30 min. The sizes range used were 0-75, 75-125, 125-180, 180-250 and 250-355 µm.

Ionic liquid pretreatment

The samples biomass were pretreated with [EMIM][Ac] at 5 wt% by mixing 0.075 g of biomass and 1.5 g [EMIM][Ac] in 1.5 mL Eppendorf tube [6]. This step was done for all size range of the samples in triplicate. The Eppendorf tubes containing the mixture were then placed into a temperature controlled shaker (BioShakeiQ, Germany). The speed of the mixing was set to 800 rpm at a controlled temperature at 85 °C for 3 hours [7]. After 3 hours, the samples were left to cool in the room temperature. After cooling, the samples were placed into a mini centrifuge (Eppendorf Centrifuge 5415 R, USA). The samples were then centrifuge at 10,000 rpm and 4°C for 10 minutes. The precipitate was form. The liquid containing [EMIM] [Ac] was removed, and the precipitate was washed at least two times with additions of distilled water in order to ensure that excess ionic liquid had been removed [7]. The samples were then dried in the drying oven at 60 °C for 48 hours.

FTIR analysis

Fourier Transform Infrared (Spectrum One FT-IR Spectrometer, Perkin Elmer) analysis was conducted to observe the biomass structure before and after pretreatment for every different particles size. All spectra were recorded in the range of 4000-400 cm^{-1} and were measured at a spectral resolution of 4 cm^{-1} and 64 scans were taken per sample.

Results and Discussion

FTIR analysis on different particles size after mechanical grinding pretreatment

FTIR analysis is a useful tool for obtaining rapid information about the functional group and chemical changes taking place in cellulose due to various pretreatments. Figure 1 shown FTIR spectra of OPF after the mechanical grinding process at different particles size of 0-75, 75-125, 125-180, 180-250 and 250-355 μm . From the figure, it was observed that the trends between all those particles sizes are quietly similar. The result obtained can be related to the type of grinder used which was hammer mill type. It was previously studied that the hammer mills give good size reduction without increasing the availability of cellulose or in other words it did not change the chemical structure of cellulose in sample biomass [8].

Although the trend obtained was practically quite similar, however, the absorption peak for smaller particles size of 75-125 μm was a little bit different compared to others. The O-H stretching vibration peak within the 3600-3100 cm^{-1} for 75-125 μm become stronger and narrower than other larger particle size ranges. Generally, cellulose structure is packed with intermolecular and intra-molecular of O-H bonding. The strong band within the 3600-3100 cm^{-1} can be concluded that there is high cellulose content for these particles size range.

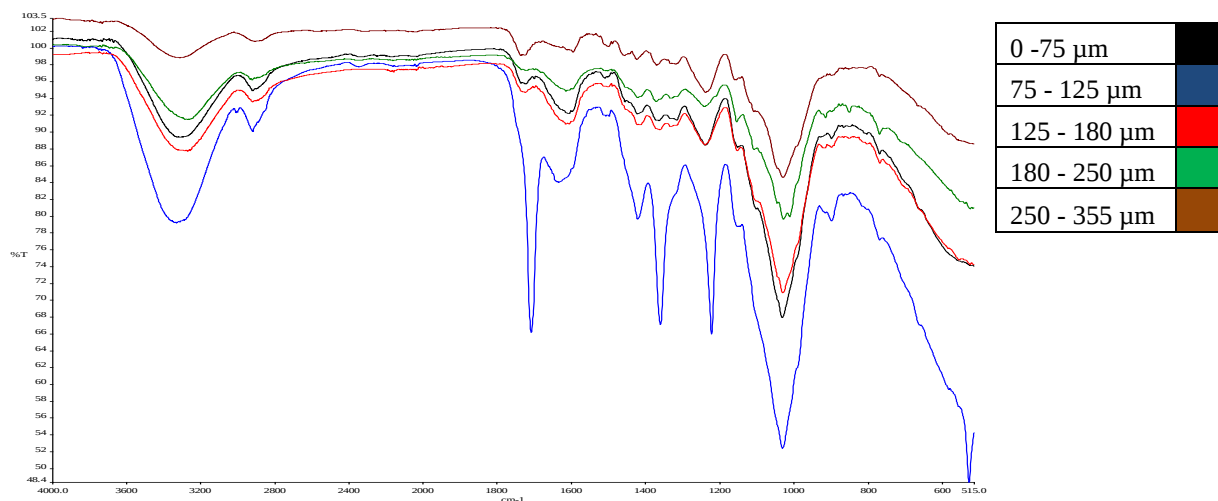


Figure 1. FTIR spectra of OPF with different particles size after mechanical grinding pretreatment

Besides, the band intensity of 1051 cm^{-1} which is corresponding of C-O stretching vibration in cellulose/hemicellulose was more resolved in spectra of $75\text{-}125\text{ }\mu\text{m}$ indicating that the cellulose rich wood fibers are richer in carbohydrates [9]. In addition, there are strong peaks form near 1700 cm^{-1} and around $1400\text{-}1300\text{ cm}^{-1}$ with respectively correspond to bending or stretching vibrations of C=O and C-H group [10]. By the analysis between the different particles size, it can be said that the particle size range of $75\text{-}125\text{ }\mu\text{m}$ was the optimum size after mechanical pretreatment. Hence, this particles size range can be selected to conduct further pretreatment with IL which has high cellulose amount due to the commonly structure characteristics of cellulose shown in FTIR spectra analysis compared to other sizes.

Comparison of FTIR analysis on different particles size before and after IL pretreatment

The comparison between before and after pretreatment by FTIR analysis was investigated to confirm whether any new functional group was generated during the interaction of OPF with IL. Figure 2 shows the FTIR spectra of OPF for particle size $75\text{-}125\text{ }\mu\text{m}$ before IL pretreatment, and after pretreatment with 1 and 3 M of IL. It was observed that the spectra generated for samples pretreated by both concentration of IL show new formation of peaks compared to the original spectra before the IL pretreatment. The band at range of $800\text{-}900\text{ cm}^{-1}$ which characterizes the C-O-C stretching at $\beta\text{-}1,4\text{-glycosidic}$ linkage is appeared after the pretreatment. The intensity of this range is very sensitive to the amount of crystalline versus amorphous structure of cellulose. The broadening of this band illustrates the amount of disordered structure (amorphous) higher [11]. The disorder arrangement of cellulose structure is expected caused by the changes in angle around of $\beta\text{-}1,4\text{-glycosidic}$ linkage and hydrogen bonding form between the sugar hydroxyl group in cellulose and ion of IL which loosen the original packing and ordered arrangement of cellulose. Besides, the band at range $1000\text{-}1200$ also resolved after IL pretreatment for both concentration which the band referred to functional groups of C-O-C and C-OH [12].

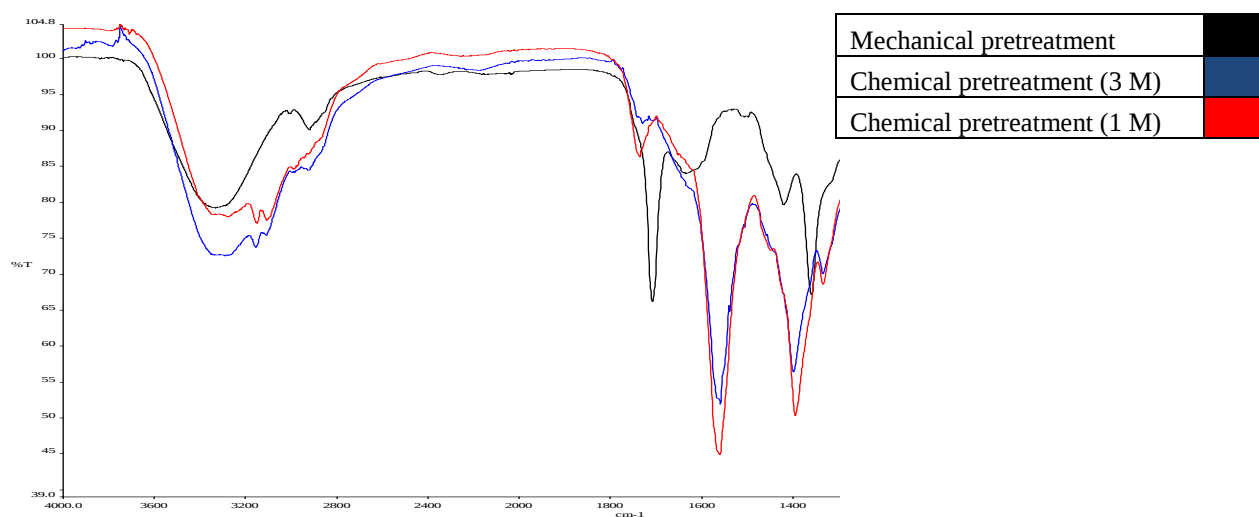


Figure 2. Comparison of FTIR spectra of OPF between before and after chemical pretreatment for size range $75\text{-}125\text{ }\mu\text{m}$

Figure 2 also illustrated that after the mechanical pretreatment (before IL pretreatment), the sample shows the presence of cellulose groups at band around 1430 cm^{-1} and hemicellulose at band near 1700 cm^{-1} . However, after the IL pretreatment for both 1M and 3M, it can be seen that the hemicellulose band of 1700 cm^{-1} has decreased and shifted to the left. The weakening of peak at 1700 cm^{-1} can be referred to the degradation of acetyl groups [12]. The peak at 1430 cm^{-1} also was originally existed in spectra of untreated biomass. However after the treating with IL, the peak was totally disappeared. Sohrab and co-worker reported this band would be strong in crystalline cellulose

and weak in amorphous cellulose [2]. The disappearance of this band showing that by IL pretreatment, the crystalline structure of sample biomass is altered to be amorphous structure.

Furthermore, there was a new peak form within 1550 cm^{-1} which relates to functional group exists in lignin. From the band formed, it can be said that by IL pretreatment, the dissolution was occurred and as a result the lignin bonding within the biomass structure was broken. Other difference characteristic which has been observed was at the band of O-H vibration, $3600\text{--}3100\text{ cm}^{-1}$. The vibration band of the treated biomass with IL for both concentrations became sharper and lower in intensity. This is due to the scission of the intra-intermolecular of O-H bonding [13]. Furthermore, from the same figure of 3, the spectra of FTIR analysis between 1M and 3M concentration of IL were quietly similar and did not show any significant different.

Conclusion

In conclusion, the particle size range of $75\text{--}125\text{ }\mu\text{m}$ is an optimum size to further pretreat with IL due to the characteristics of cellulose observed in FTIR spectra. The comparison between the cellulose structure of OPF between mechanical (before IL pretreatment) and chemical (after IL pretreatment) also has been studied. Based on the result, it shows that the chemical structure of cellulose was disrupted by formation of O-H bonding between the hydroxyl of cellulose and ion of IL during the dissolution time with IL. As a result, the cellulose network broken and less in crystalline structure. In bioethanol production from LB feedstock, the cellulose crystalline structure is a concern because it may affect the sugar yield during the enzymatic hydrolysis.

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